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FINAL REPORT

AFOSR-TR-89-1398

PROJECT: RAMAN STUDY OF SOLID STATE REACTIONS

SPONSOR: USAFOSR

PERIOD: September 1, 1978 to August 31, 1979

GRANT #: AFOSR-78-3676

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During the period 9/1/78 to 8/31/79, a considerable amount of work was done towards understanding the nature of reactions in solids. The first step in the investigation of the solid state reactions was the synthesis and the characterization of the materials. Methyl-p-dimethylaminobenzenesulfonate, p-trimethylammoniumbenzene sulfonate, tri-o-thymotide were synthesized and characterized by their Raman spectra. Other compounds proposed for study were, trans-cinnamic acid and p-nitrophenol, the phonon spectra and the internal vibration spectra of which in two crystalline modifications were studied. Another matrix which we proposed for study was cyclodextrin whose Raman spectra were also studied.

Solid state photodimerization of two modifications of trans-cinnamic acids in pure crystals was investigated. The Raman spectra of both the phonon region and the internal vibration region were studied as a function of photodimerization. Figure 1 shows the Raman spectra in phonon region of the trans-cinnamic acids and their respective dimers. In this photodimerization ^{was shown} we investigated using the phonon spectra, the mechanism of the product lattice formation, i.e. whether the reaction proceeds by a homogeneous mechanism with the formation of a solid solution between the reactant and the product or by a heterogeneous reaction where the product forms its own lattice.

As was suggested in the proposal, phonon spectra proved to be conclusive and it was found that the photodimerization proceeds by a heterogeneous mechanism, i.e. no solid solution forms between the reactant and the product. The major thrust of the research has been to derive a dynamical concept of reactivity by considering the role of phonon motions of the lattice in determining reactivity. Large amplitude phonon motions

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are the analogs of molecular collisions in the gas phase. The two crystalline modifications of trans-cinnamic acid differ in the degree of reactivity. The β -form is more reactive than the α -form. It can be seen from figure 1 that the β -form has a very low lying phonon transition ($\sim 27 \text{ cm}^{-1}$) where as for the α -form the lowest phonon transition is at $\sim 52 \text{ cm}^{-1}$. In the 27 cm^{-1} motion the molecules execute large amplitude oscillations which may account for enhanced reactivity. These findings on trans-cinnamic acid were presented at the American Chemical Society Symposium on April 2, 1979 in Honolulu.

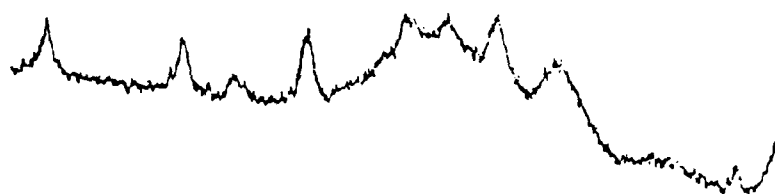
The thermal rearrangement reaction of methyl-p-dimethylaminobenzene sulfonate (MSE) in pure crystal to form the product p-trimethylammonium benzene sulfonate Zwitterion (ZWT) was also investigated during this period. Detailed studies of the phonon spectra as well as the internal vibration spectra were made as a function of the percentage rearrangement using polycrystalline samples as well as single crystals in different orientations. Figure 2 shows the spectra for the reactant (top Spectrum), the 40% conversion sample (middle spectrum) and the product (bottom spectrum) for the phonon region. Except for the spectral intensity changes due to a difference in orientation, the spectra of the 40% conversion sample can be explained as consisting of unperturbed bands of both the reactant and the product. The same is true for samples of other percentage conversion. From this result we conclude that no solid solution between the reactant and the product is formed when the reaction proceeds. In other words the reaction proceeds by a heterogeneous mechanism. This observation is consistent with the following mechanism:

An important aspect of a dynamical model is to determine specificity in phonon induction of solid state reactions. In order that a large population of selective and coherent vibrational excitation can be achieved to study its effect on reactivity it is necessary that vibrational relaxation be slow. For this reason it is important to investigate and characterize vibrational relaxation and dephasing in organic solids. This study was undertaken during the tenure of the Air Force grant. Two proto systems were investigated. The dephasing of a localized internal vibration of the naphthalene crystal was investigated by studying the temperature dependence of the line width, the line shape and the line frequency. It was found that at liquid helium temperatures the contribution to dephasing due to physical processes which are of interest to us is almost negligible. The observed dephasing can entirely be explained due to inhomogeneities. Even at higher temperatures the T_1 -relaxation time which is responsible for decay of the vibrational excitation is very long. This result is extremely encouraging from the point of view of being able to selectively pump a high degree of vibrational excitation of a given mode. Another system in which we have studied vibrational relaxation is p-bromochlorobenzene. This system in crystalline state exhibits orientational disorder and our motivation was to study phonon relaxation in a structurally disordered system. The work revealed that even in a structurally disordered system for which both anharmonic interactions and structural disorder provide scattering mechanisms, the study of temperature dependence of line-widths can be used to derive information on phonon relaxations. To discern the effect of disorder, the result on p-bromochlorobenzene

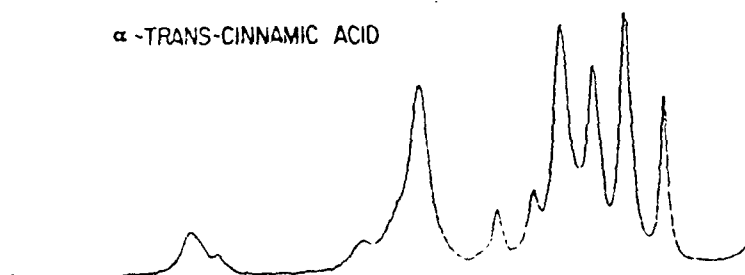
was also compared with that on isomorphic p-dichlorobenzene crystal which exhibits no structural disorder. It was found that for both these p-dihalobenzenes the phonon relaxation at liquid helium temperatures is $>10^{-10}$ sec.

On the side of the instrumentation progress has also been made. An automation system has been introduced in which experiments are controlled by a MicroNova computer. The data are obtained and digitally processed. For larger computations the data can be transferred from MicroNova to the University computing facility through a modem. MicroNova will also control the multichannel detection system acquired through the Air Force grant. This system is in the process of being used for time resolved study of solid state reactions so that a large spectral region can be sampled in milliseconds. To improve the signal to noise ratio in this multichannel detection we are making several modifications. An iodine filter is being assembled which can be used with the $5145\overset{\circ}{\text{Å}}$ laser excitation to reduce the background. We are also in the process of building a background rejection optical-filter for cases where we need to use other excitation wavelengths. This filter consists of two gratings which are put together in a subtractive mode. The first grating disperses the scattered radiation. A stopper in the path of the dispersed beam blocks the laser light and the shorter wavelengths, but passes all the longer wavelengths which then are combined by the second grating and focused on the slit of the 14018 double monochromator.

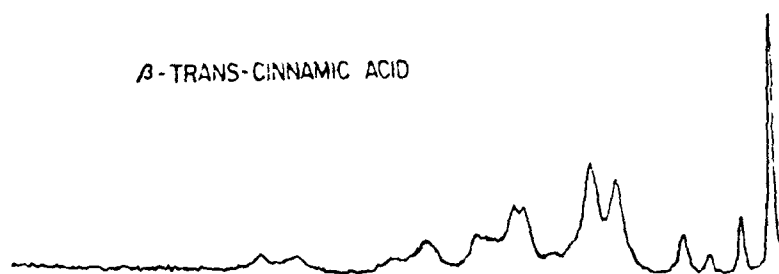
α -TRUXILLIC ACID



α -TRANS-CINNAMIC ACID



β -TRANS-CINNAMIC ACID



β -TRUXINIC ACID

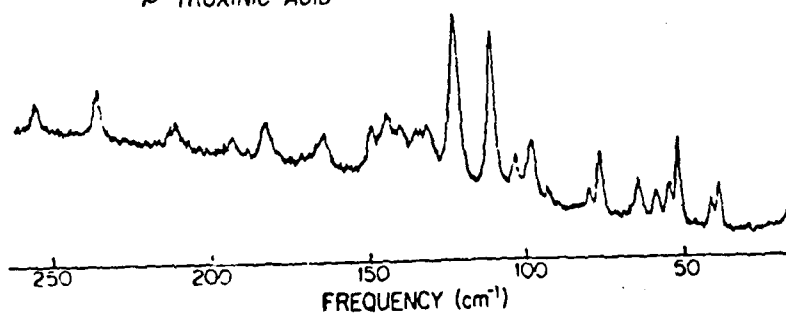


Figure 1

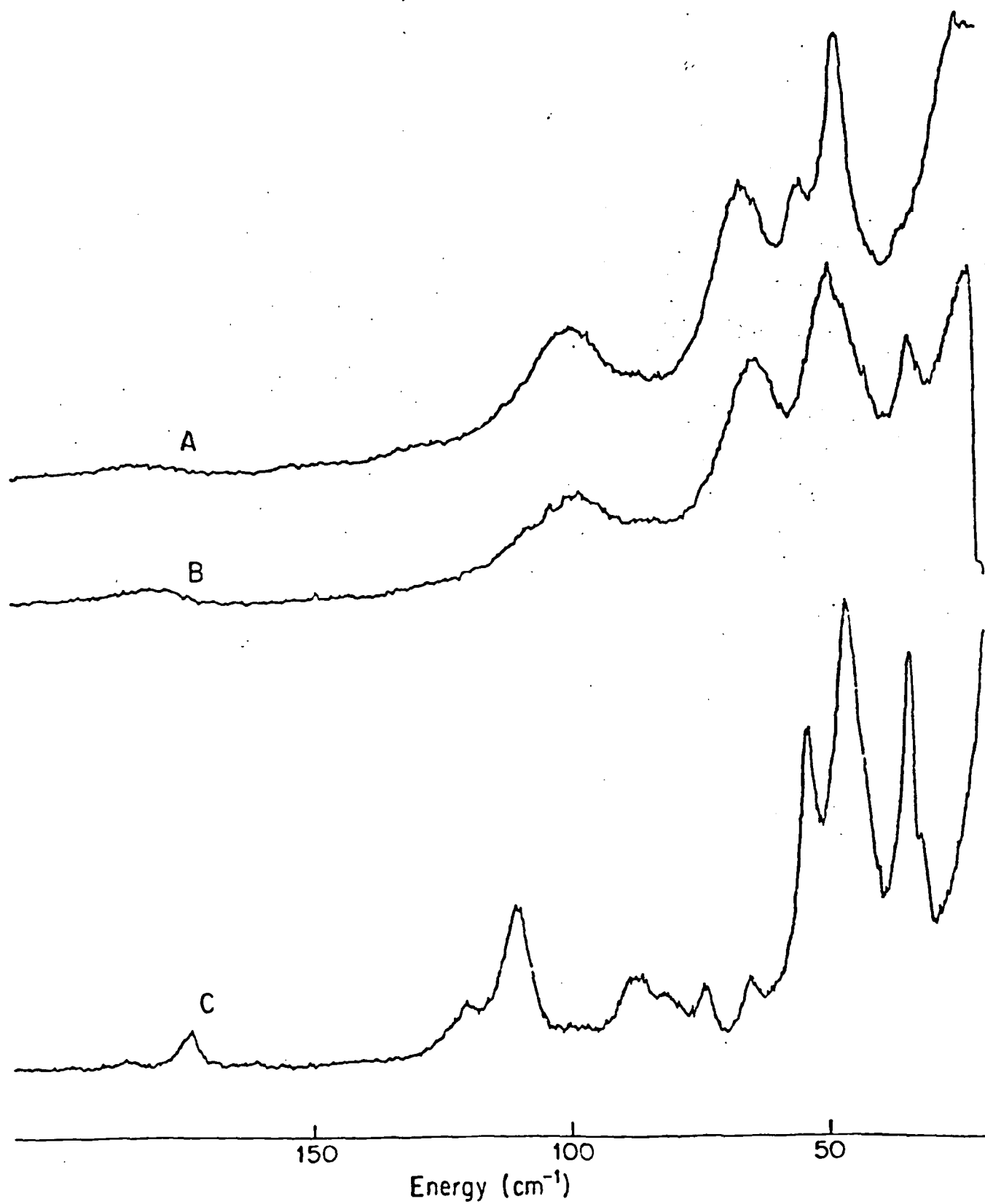


Figure 2

SUMMARY OF THE ACCOMPLISHED RESEARCH UNDER AFOSR-78-3676

(Period 9/1/78 - 8/31/79)

PUBLICATIONS

1. "Vibrational Relaxation in a Structurally Disordered Solid: Temperature Dependence of Raman Active Phonons in p-Bromochlorobenzene and p-Dichlorobenzene", P. N. Prasad, and R. V. Smith, J. Chem. Phys. 71, 4646 (1979).
2. "Vibrational Dephasing in Organic Solids: Temperature Dependence of a Localized Raman Active Internal Mode of Naphthalene", L. A. Hess and P. N. Prasad, J. Chem. Phys. Jan. 1, 1980 (scheduled publication date).
3. "Vibrational Relaxations and Dephasing in Organic Solids", P. N. Prasad. Mol. Cryst. Liq. Cryst. (in Press).
4. "Raman Phonon Spectroscopy of Solid State Reactions: Thermal Rearrangement of Methyl-p-Dimethylaminobenzene Sulfonate in Solid State", K. Dwarakanath and P. N. Prasad, Submitted for publication in J. Am. Chem. Soc.

ORAL PRESENTATIONS:

1. "Laser Raman Study of Solid State Reactions", P. N. Prasad. Presentation on April 2, 1979 at the American Chemical Society Symposium in Honolulu.
2. "Laser Raman Study of the Thermal Rearrangement of Methyl p-Dimethyl-Aminobenzene Sulfonate in Solid State", K. Dwarakanath, R. V. Smith and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.
3. "Vibrational Relaxation and Dephasing of Raman Active Modes in Molecular Solids and Crystalline Molecular Complexes", L. A. Hess and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.